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Receptors for anions

N A Itsikson, Yu Yu Morzherin, A I Matern, O N Chupakhin

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Abstract. The published data on receptors for anions with different geometry are generalised. Special attention is given to the analysis of binding abilities of organic ligands. Structural features of complex-forming agents and their properties are considered. The bibliography includes 147 references.

I. Introduction

Despite the fact that anions play an important role in different chemical [1] and biological [2] processes, including catalytic ones,[3] as well as in medical studies,[4] the coordination chemistry of these species is yet to be properly generalised in contrast to the chemistry of the ligands binding cations or neutral molecules.[5] Past years witnessed a swift increase in the number of papers devoted to the synthesis and properties of receptors for anions (see *e.g.* reviews [6–9] and references cited therein). Recently published reviews [10, 11] only summarise the data on the ability of certain classes of organic compounds to extract wide range of anions. In the present review, our attention is drawn to the functional-oriented design of complex-forming agents for anions. The goal of this paper is to demonstrate what functional groups should be introduced into a molecule as a basis for the directed synthesis of selective receptors for negatively-charged species and to systematise various data on the synthesis of ligands that can selectively extract certain types of anions.

Anions differ from each other not only in their charge, but also in the size and geometry. For example, halide anions have spherical shape, SCN^-, N_3^- are linear, COO^-, NO_3^- are planar, $H_2PO_4^-$, HSO_4^- are tetrahedral, *etc*. Consequently, one can use different neutral and positively charged species for binding anions. The main criteria of the ability of a compound to act as a receptor is the possibility of hydrogen bonding to anions.[12] That is why the structure of a ligand possessing receptor ability with respect to anions is not strictly defined, to this end one can use (thio)ureas,[13–26] amines,[27–30] amides,[31–39] thioamides,[40] sulfonamides,[41] indoles,[42, 43] pyrroles,[44–50] imidazoline and guanidine cations [51] and so on. For example, the best receptors [52] for the binding of the anions F^-, AcO^-, $H_2PO_4^-$, ClO_4^-, Cl^-, Br^- and I^- are urea and thiourea derivatives, which what was shown both experimentally,[53] and by the calculations of the degree of affinity of these ligands to spherical, tetrahedral and planar anions.[54, 55]

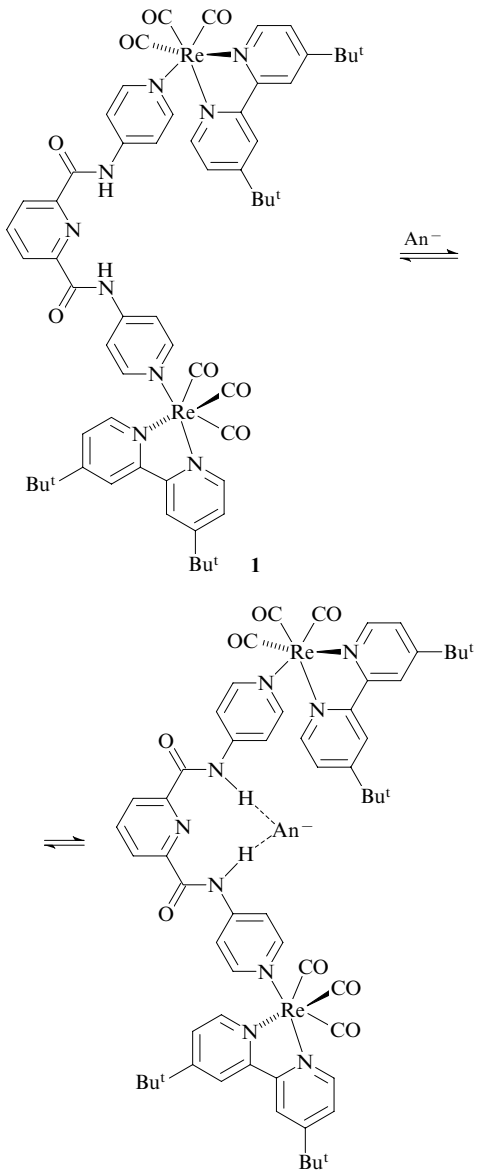
II. Molecular recognition of spherical anions

The selectivity of ligands with respect to anions as well as stability of the complexes formed are influenced by the electrostatic and structural factors. Only those compounds that have molecular cavities with dimensions of the size of a spherical anion and containing functional groups capable of forming H-bonds are suitable ligands for the negatively charged species. One of the examples of receptors for anions is the rhenium complex of pyridyl-containing ligand **1** with amide NH groups.[56] This compound is characterised by high affinity to halide anions: the binding constants † with ions F^-, Cl^-, Br^- and I^- are equal to 3.82×10^5, 4×10^4, 4×10^4 and 1.49×10^5, respectively.

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† Hereinafter, the names of the binding constants (K) and association constants (K_{ass}) are given according to the original papers, dimensionality is litre mole^{-1}.



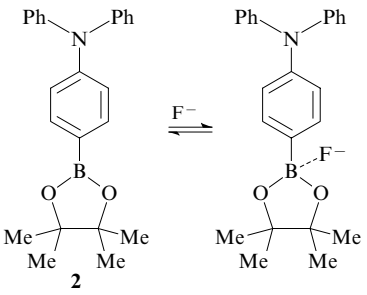
An is anion.

Compound **1** exhibits high binding ability with respect to halide anions due to the cumulative effect of electrostatic attraction and hydrogen bonding as well as due to the presence of molecular cavities of appropriate sizes.

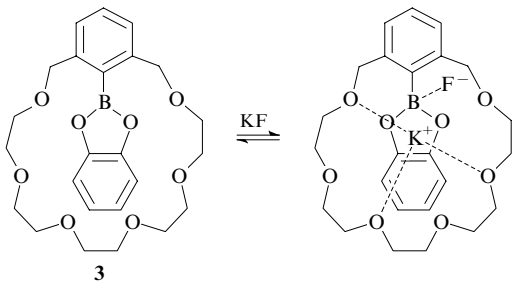
1. Binding of the fluoride anion

The distinctive features of the fluoride anion compared to other halide anions are its small ionic radius, high electronegativity of the F atom and ability of solvation by some solvents. By this reason, this anion is discussed in a separate section.

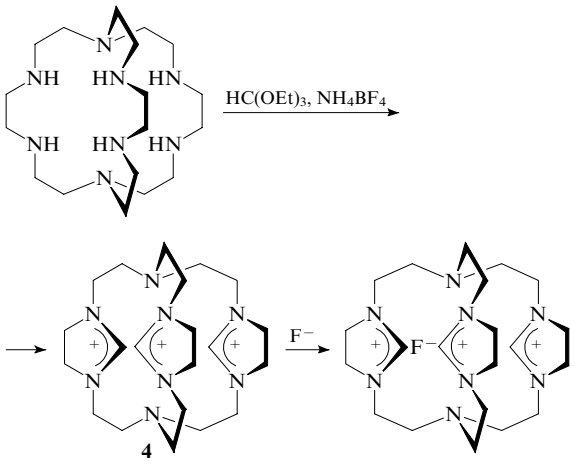
High affinity to the fluoride ion of the boron atom allows one to use boron derivatives as sensors to this anion. For example, triarylamine **2** containing a boronate group [57] is a very promising ligand for these purposes. It is characterised by the selectivity of complexation as well as by high binding constant ($K = 10^7$) with the fluoride anion compared to the analogous parameters for other halides.



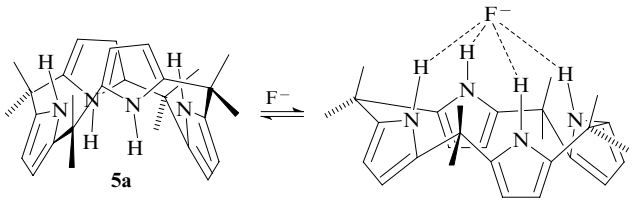
In the reaction of KF with boron derivative **3**, spontaneous coordination of the potassium cation by the oxygen atoms of the crown-ether ring occurs together with the binding of the fluoride anion to the boron atom.[58] It should also be mentioned that this compound cannot act as a ditopic receptor [59] for KCl and KBr, as in this case it binds only the potassium cation.



Receptor **4** based on imidazolidinium trication exhibits unprecedented affinity and high selectivity for the binding of the fluoride anion ($K = 10^{13}$).[60] Small cavity size of this molecule can accommodate only anion with small ionic radius (1.33 Å).



Calix[4]pyrroles represent another group of ligands capable of interacting only with F^- (Ref. 48). It was shown [61, 62] that such binding is accompanied by the formation of strong H-bond NH···F^- and changes in the geometry of calixpyrrole **5a** molecule: the *1,3-alternate* conformation transforms to the *cone*.

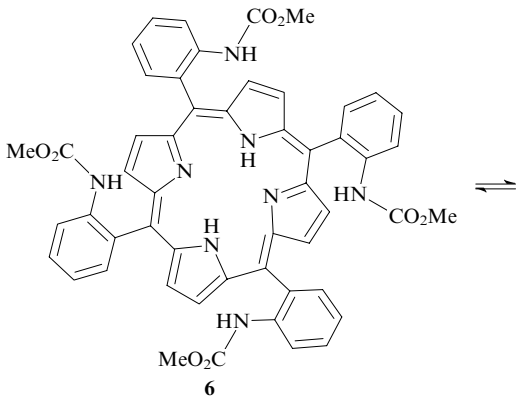


5a

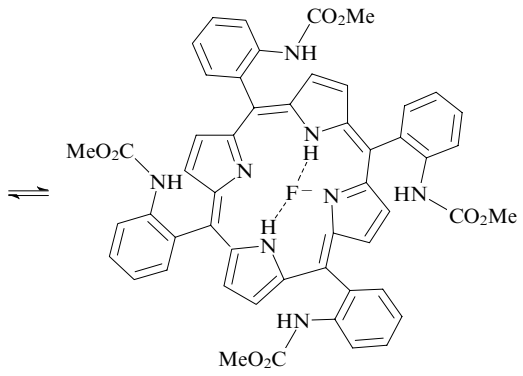
High binding constant to the fluoride anion (10^5) for receptor **5a** compared to the analogous parameter for other halide anions ($10-10^2$) allows one to consider this compound as a selective receptor for the anion F^-. However, upon the increase in the number of pyrrole rings and consequently in the size of the molecular cavity of the calixpyrrole macrocycle, the complexing ability of receptor with respect to the halide ions increases in the series $F^- \ll Cl^- < Br^- < I^-$ (*cf.* Ref. 1).

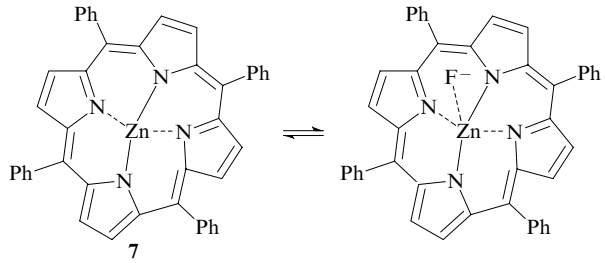
Analogous dimeric[63] and hybrid calixarene systems in which one or several pyrrole rings are replaced by similar heterocyclic fragments such as thiophene, furan, bithiophene and bipyrrole do not exhibit selectivity in the interaction with negatively charged species.[64] They bind anions of not only spherical shape, but also planar ones (*e.g.* $PhCO_2^-$) and even tetrahedral ones (*e.g.* $H_2PO_4^-$).

It was found that porphyrins and metalloporphyrins can be used for the binding of the fluoride anion, the mechanism of such interaction depending on the nature and structure of the porphyrin system.[65] Thus porphyrin **6** coordinates F^- through the formation of H-bonds ($K = 2.6 \times 10^4 - 2.5 \times 10^5$), while in the case of complex **7** fluoride anion interacts with zinc cation according to the donor–acceptor mechanism ($K = 7.7 \times 10^2$).[66]



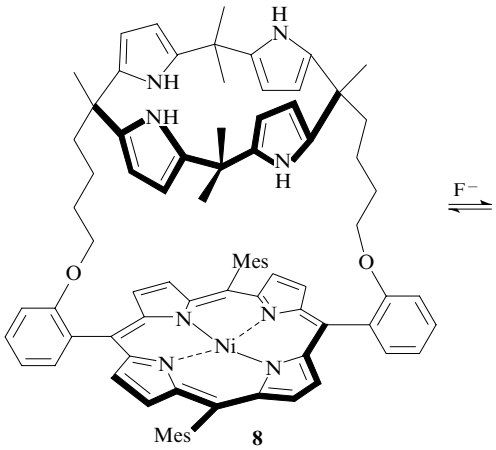
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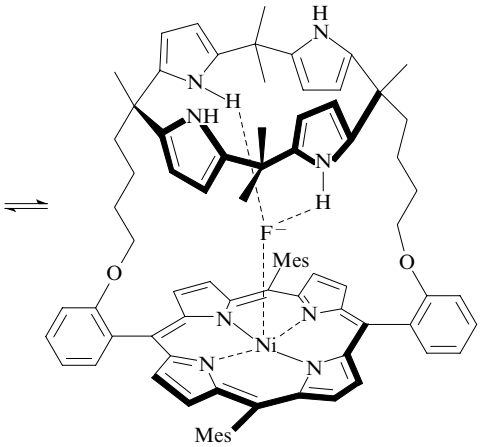


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Compound **8**, which combines calixpyrrole (in *1,3-alternate* conformation) and porphyrin macrocycles, exhibits high receptor ability with respect to the fluoride ion in the presence of other halide anions.[67]

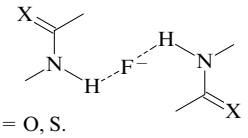


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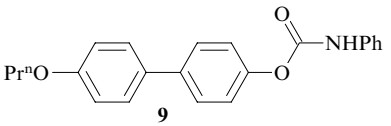
Mes = 2,4,6-$Me_3C_6H_2$.

Compounds containing amide groups, (thio)urea fragments or their combination selectively bind the fluoride anion due to the formation of strong H-bonds with protons at the nitrogen atoms.

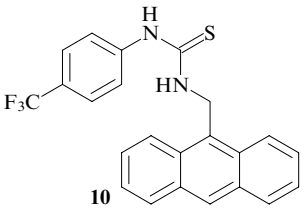


X = O, S.

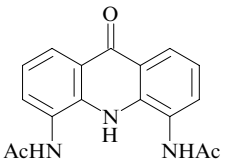
This class of receptors is represented by compounds with both linear (**9**–**14**) and cyclic (**15**–**17**) structures. The



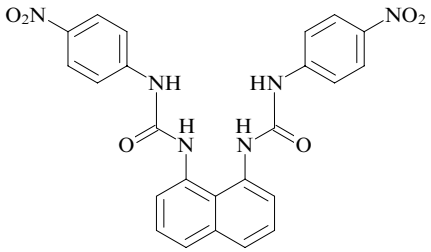
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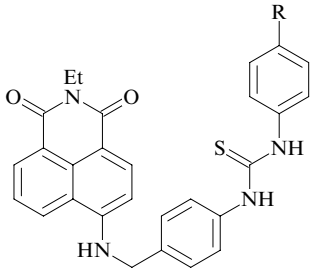
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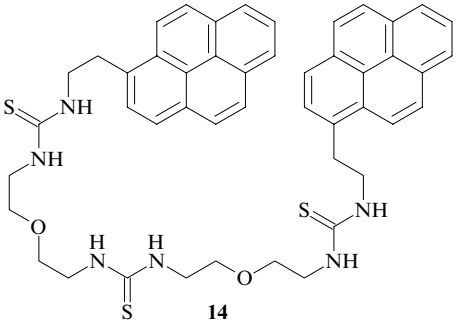


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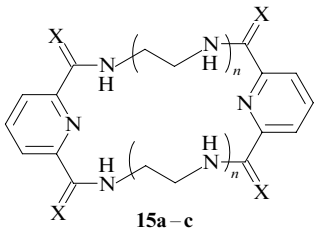


13a,**b**

R = H (**a**), CF_3 (**b**).

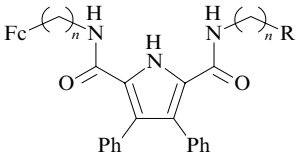


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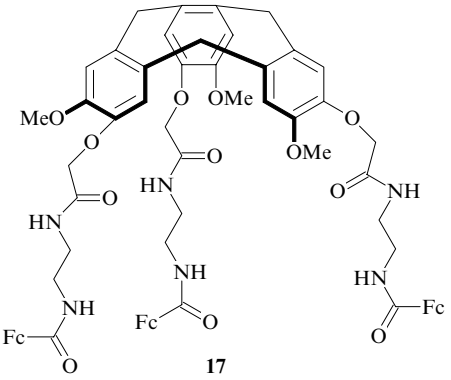
15a–**c**

n = 1: X = S (**a**), O (**b**); *n* = 3, X = O (**c**).



16a–**d**

n = 0: R = Fc (**a**), Ph (**b**);
n = 1: R = Fc (**c**), Ph (**d**);
Fc is ferrocenyl.



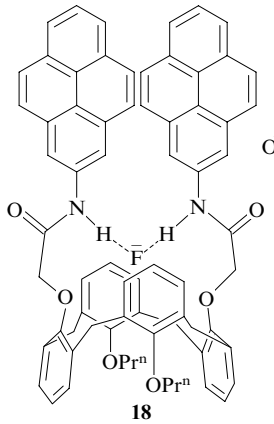
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original papers describing the synthesis of such ligands as well as measured binding constants to the fluoride anion are cited in Table 1.

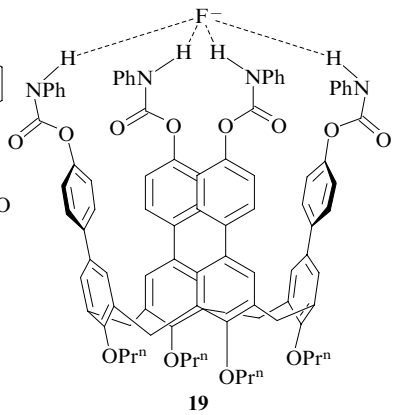
Table 1. Binding constants of fluoride anion by receptors **9**–**18**.

Compound	*K*	Ref.
9	9582	68
10	2.5×10^3	69, 70
11	–	71
12	–	15
13a	6×10^3	72
13b	2.5×10^4	72
14	5111	73
15a	10^4	74
15b	8×10^2	74
15c	10^3	75
16a–**d**	$2.0 \times 10^1 - 2.3 \times 10^2$	76
17	10^2	77

Calixarene is a very suitable scaffold for the formation of preorganised receptors for different anions. The modification of the lower or upper rim of the calixarene macrocycle by amide fragments results in the formation of selective complex-forming agents for the fluoride anion. It is noteworthy that calixarenes can have both *1,3-alternate* (compound **18**), and *cone* conformations (**19**).[68, 78]



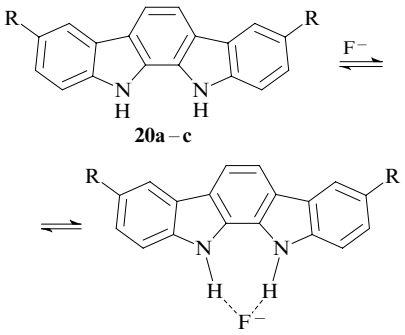
18



19

The ligands for the effective binding of the fluoride anion can also be obtained by the combination of crown-ether and calixarene macrocycles in one molecule.[79]

To ensure the fixed position of NH groups in space, one can build polycyclic systems on the basis of nitrogen-containing heterocycles. For example, indolo[2,3-*a*]carbazole **20a**–**c** derivatives bind the fluoride anion with the formation of 1 : 1 complexes.[42]



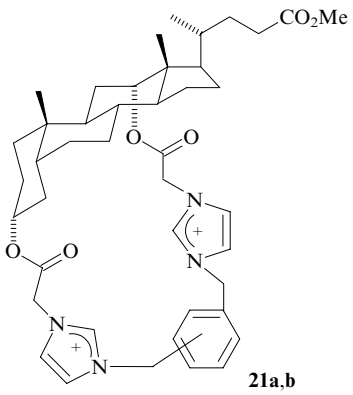
20a–c

R = H (**a**), Me (**b**), Br (**c**).

The association constant does not virtually depend on the nature of the substituent in the carbazole ring:

Compound	**20a**	**20b**	**20c**
log K_{ass}	4.7	4.7	5.0

Novel cyclic receptors **21a**,**b** with the steroid skeleton containing two imidazole rings connected by a bridge exhibited selectivity with respect to the fluoride or chloride anions.[80]



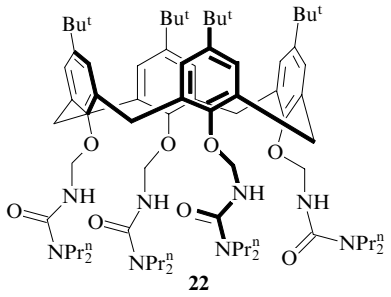
21a,**b**

Isomers: (**a**) *meta*, (**b**) *para*.

In this case, the decisive role is played by the structure of the phenylene substituent. Thus ligand **21a**, the *m*-xylene derivative, binds the fluoride anion, and the isomeric *p*-xylene derivative is the receptor for the chloride anion. However, an acyclic non-steroidal receptor for the latter is known,[81] which is based on diimidazole derivative of *m*-xylene.

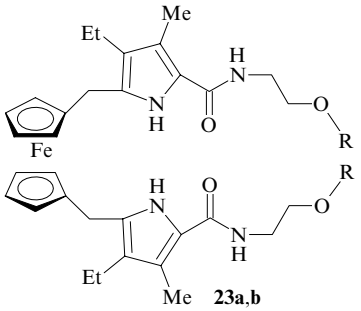
2. Binding of the chloride, bromide and iodide anions

The directed design of receptors for other halide ions is based on the following requirements: the size of the molecular cavity of a ligand should be comparable to the radius of the anion, the molecule should possess groups capable of forming strong H-bonds. Slight difference in the ionic radii (0.181 and 0.196 nm for the anions Cl^- and Br^-, respectively), as well as in the values of free energy make the problem of selective recognition of chloride and bromide anions difficult to solve.[82] Thus the association constants of these anions with receptors **22** are of the same order of magnitude (230 and 221 for the anions Cl^- and Br^-, respectively).



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An example of binding by the carboxamide-substituted ferrocenes **23a**,**b** of the chloride anion in the presence of bromide anions is documented.[83]



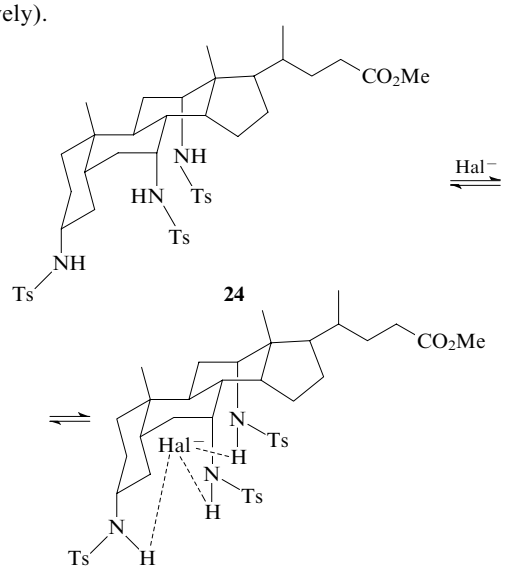
23a,**b**

R–R = $(CH_2)_2$ (**a**),
R = Me (**b**).

However, in this case, too, the formation of complexes with both anions is possible, while the selectivity is determined by the solvent polarity, which greatly influences the association constant (*cf*. Refs 48, 76 and 83). Scherer *et al*.[83] have measured the association constants of the ions Cl^- and Br^- by the receptors **23a**,**b** in acetonitrile:

Compound	K_{ass}	
	Cl^-	Br^-
23a	9031	857
23b	1260	66

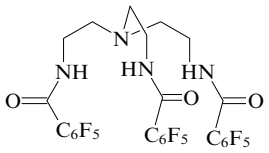
It was found[84] that steroid-like ligand **24** is also more prone to the interaction with the chloride anion compared to the bromide anion ($K_{ass} = 10^6$ and 9.2×10^4, respectively).



24

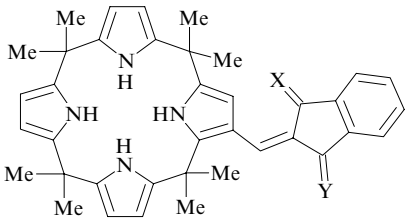
Hal = Cl, Br.

Such a spacial disposition of the NH groups in tripodal ligand **25a** favours binding of the halide anions.[85]



25a

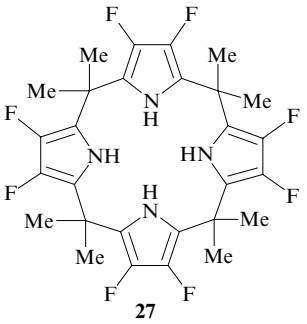
The examples of binding of chloride anion by the macrocycles containing not only amide, but also pyrrole fragments, are also described in literature.[47,86] Thus the recognition ability of 2-methylideneoctamethylcalix[4]pyrroles **26a–d** with respect to the chloride anion is 50 times larger than that of unsubstituted calixpyrrole.[87]



26a–d

X = 2 H, Y = $C(CN)_2$ (**a**); X = Y = O (**b**); X = O, Y = $C(CN_2)$ (**c**); X = Y = $C(CN)_2$ (**d**).

Analogous enhancement of complexing properties was also observed for fluorinated derivative of calix[4]pyrrole **27**.[88]

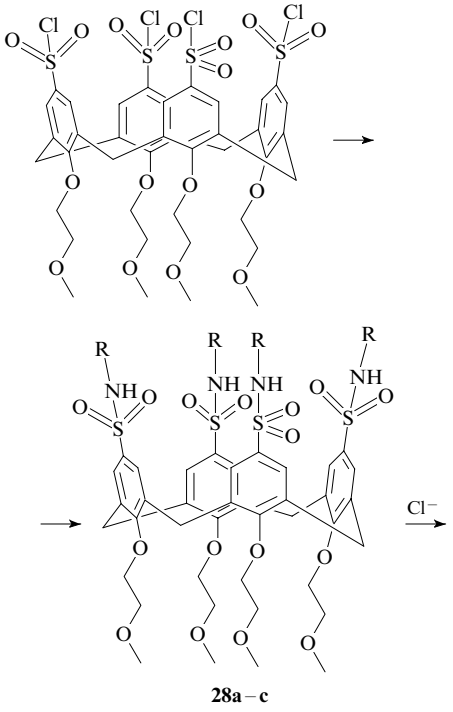


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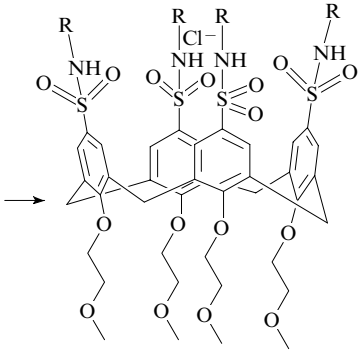
Recently synthesised[89] calixpyrroles containing amide groups in the molecule effectively bind halide ions. It should be mentioned that upon their interaction with the fluoride anion, only 1 : 1 complexes are formed, with the chloride anion, 1 : 1 and 2 : 1 complexes and with bulkier bromide anion, only 2 : 1 complexes.

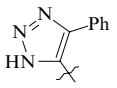
Calixarenes are good receptors for the anions Cl^- and Br^-. Modification of macrocycles at the upper rim with functional groups capable of forming H-bonds opens new possibilities for the molecular design of the anion-complexing agents.

It was shown that sulfonamidocalix[4]arenes **28a–c** form stable complexes with the anion Cl^-. Thus the binding constant for compound **28a** is equal to 3.6×10^2, while the presence of alkylamide or triazole fragments in the upper rim of the calixarene macrocycle leads not only to the increase in the molecular cavity, but also influences the stability constants of the complexes formed ($K = 0.9 \times 10^3$ and 1.25×10^3 for calixarenes **28b**,**c**).[90,91]

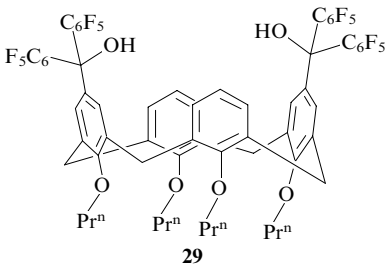


28a–c



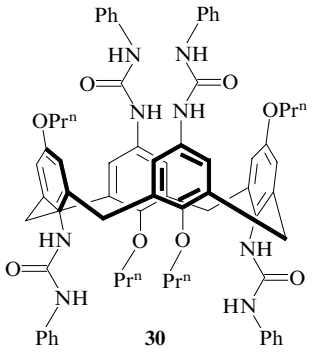
R = Pr^n (**a**), $(CH_2)_2NHAc$ (**b**),  (**c**).

A selective receptor of the bromide anion was obtained upon modification of the upper rim of the calixarene matrix with perfluoroaryl substituents.[92] The association constant for receptor **29** with respect to the anion Br^- is equal to 480, while it is only 90 for the acetate anion.

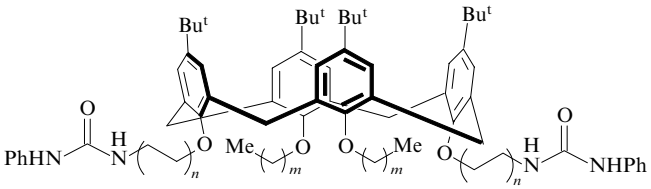


29

The introduction of urea or thiourea fragments into calixarenes is the most widely used way of synthesis of ligands for the halide anions. Such receptors are based on calix[4]arenes with different structures both in *1,3-alternate* (compound **30**),[93] and *cone* conformations, containing

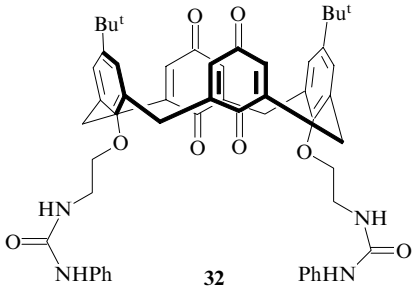


30

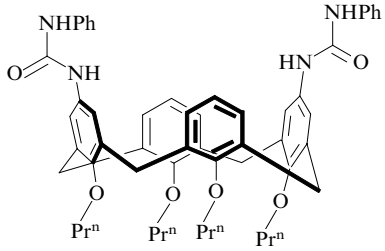


31a,**b**

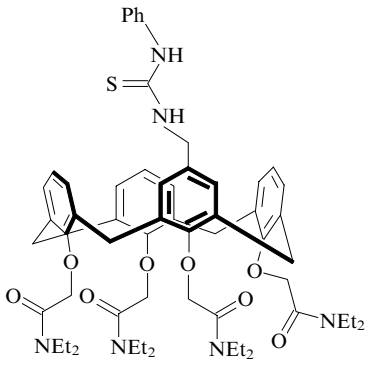
$n = m = 2$ (**a**); $n = 1$, $m = 0$ (**b**).



32



33



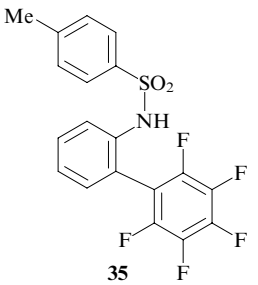
34

(thio)urea groups in the lower (**31**, **32**)[94–96] or upper (**33**, **34**)[93,97] rim. Although ureidocalixarenes have high recognition ability, they are not selective with respect to particular anions (Table 2).

Table 2. Stability constants of complexes of ureidocalixarenes **30**–**34** with the halide anions.

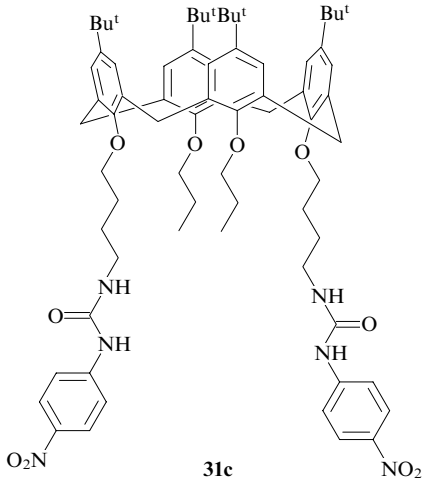
Compound	K		Ref.
	Cl^-	Br^-	
30	4.7×10^3	1.5×10^3	93
31a	7.1×10^3	2.6×10^3	94
31b	2.5×10^3	1.6×10^3	95
32	8.3×10^2	2.8×10^2	95, 96
33	4.6×10^3	1.4×10^3	93
34	160	< 5	97

Several interesting examples of the halide ion binding by compounds that are devoid of molecular cavities are also described. Thus *N*,*N*′-dibutyl-4,6-dihydroxyisophthalimide reacts selectively with Cl^- and can be used for the transportation of this anion though EYPC-liposomes.[98] Sulfamide **35** in solution exhibits the recognition ability with respect to the halide anions:[99] the constants of its binding to anions Cl^-, Br^- and I^- are equal to 30 ± 3, 20 ± 2 and 34 ± 6, respectively.



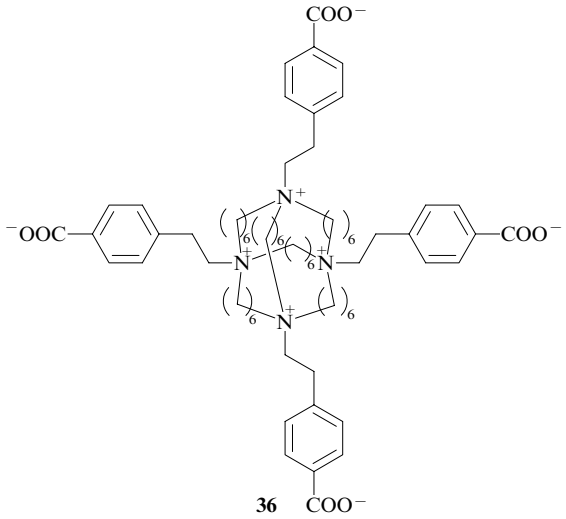
35

Due to the large ionic radius (0.220 nm) and low electronegativity of the iodine atom, only a small number of receptors for the anion I^- are known. One of few ligands exhibiting selective binding ability with respect to the iodide anion ($K = 2.5 \times 10^4$) is calix[6]phyrin.[100] Calix[4]arene **31c** containing ureide fragments in the lower rim can easily form H-bonds with the iodine anion and can successfully be used as a ditopic receptor for the simultaneous recognition of Li^+ and I^- ions (Ref. 101).



31c

High affinity with respect to the iodine anion ($K = 6.5 \times 10^3$) is also exhibited by polyamine **36**, which has an intermolecular cavity of a suitable size.[102]

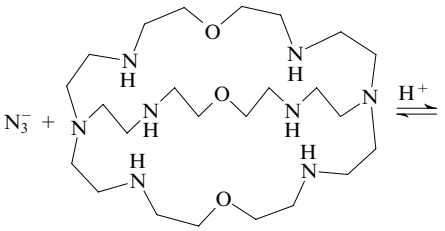


36

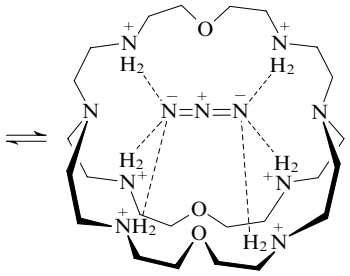
III. Coordination chemistry of non-spherical anions

1. Binding of linear anions

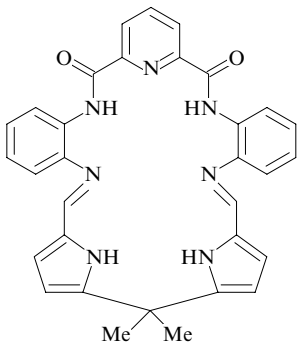
The matching character of linear anions (*e.g.* CN^-, N_3^-) and the energies of their binding depend on the properties of anions and the disposition of the binding sites in the 'host' molecule. For example, cryptand **37** is not a preorganised ligand, but it undergoes conformational changes upon binding to the azide anion.[103]



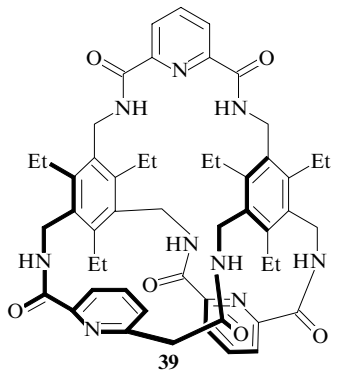
37



Several examples of complexation with the cyanide anion by both open-chain[56] and cyclic ligands **38**[104] and **39**[105] containing pyridine-2,6-dicarboxamide fragment are documented. For example, the binding constant of CN^- ion by complex **1** is equal to 8.8×10^5 (Ref. 56), and by complexes **38** and **39**, 1.2×10^4 and 1.15×10^2, respectively.



38



39

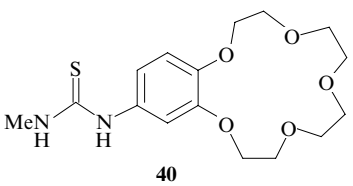
2. Recognition of planar anions

In the biological processes, an important role is played by planar carboxylate and nitrate anions; thus, the design of receptors for such anions is of great importance. Acetate can be bound to open-chain and cyclic compounds containing one or several (thio)amide groups and fragments of (thio)urea (*e.g.*, compounds **40**–**44**), also in combination with nitrogen-containing heterocycles (pyrroles and pyridines) (**1**, **13a**,**b**, **15a**,**b**, **38**, **39**, **45**–**47**).

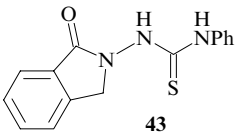
Table 3 cites the original papers on the synthesis of such receptors as well as their binding constants with the acetate ion.

Table 3. Binding constants of the AcO^- anion.

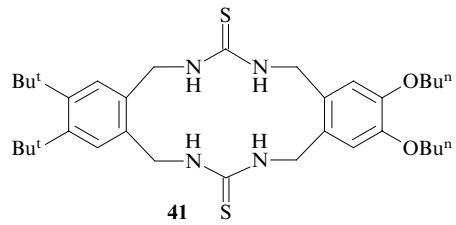
Compound	*K*	Ref.
1	6.3×10^2	56
13a	7.9×10^3	74
13b	1.0×10^4	74
15a	1.4×10^4	74
15b	2.6×10^6	74
38	3.8×10^4	104
39	3.0×10^2	105
40	2.2×10^3	106
41	2.2×10^3	107
42	1.2×10^5	73
43	2.7×10^5	108
44	–	109
45	1.5×10^5	110
46	4.8×10^2	111
47	5.6×10^2	112



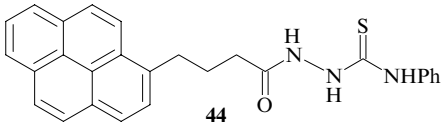
40



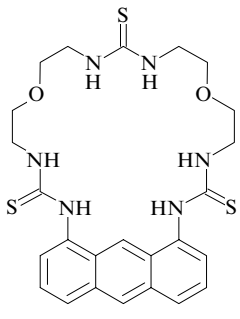
43



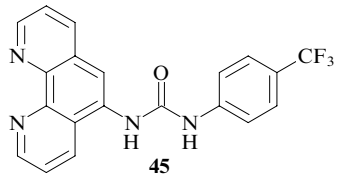
41



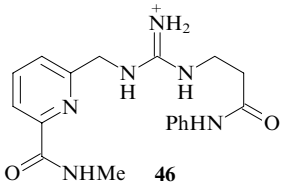
44



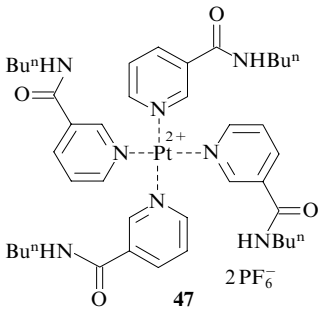
42



45

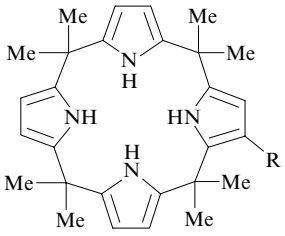


46



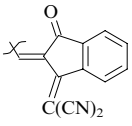
47

Spatially preorganised macrocycles are suitable ligands for the recognition of the AcO^- anion. Porphyrins and their analogues exhibit high capability to coordinate carboxylate anions both in the solution and in the solid state.[65, 66, 113] For example, binding constants measured[114] for tetrapyrrolomacrocycles **5b**, **26c** and **26e** with the acetate anion are equal to 5.0×10^2, 1.2×10^3 and 1.4×10^3, respectively.

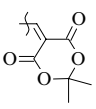


5b, **26c**,**e**

R = CHO (**5b**),

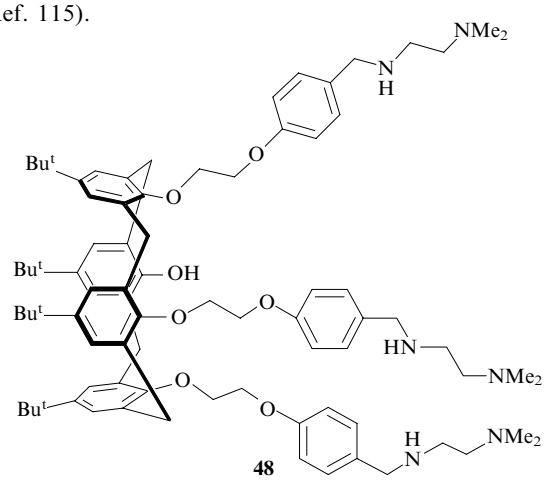


(**26c**),



(**26e**).

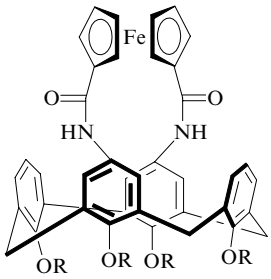
Calix[4]arenes that contain such functional groups as a polyamine chain,[115] a thiourea fragment,[116] a formyl fragment,[117] an amide group,[77] an amidoferrocene moiety, *etc.*, are widely used for the complexation of the acetate anion. Thus for calix[4]arene **28c** the binding constant is equal to 5.0×10^2 (Ref. 90), while for derivative **48**, 1.9×10^3 (Ref. 115).



48

Compounds **49a**,**b** act as electrochemical sensors for carboxylate anions selectively binding them in the presence of $H_2PO_4^-$ and Cl^- (Ref. 118).

It should also be mentioned that the binding constants for the benzoate and acetate anions by receptors **49a**,**b** depend on the nature of the alkoxyl group in the lower rim of calixarene.

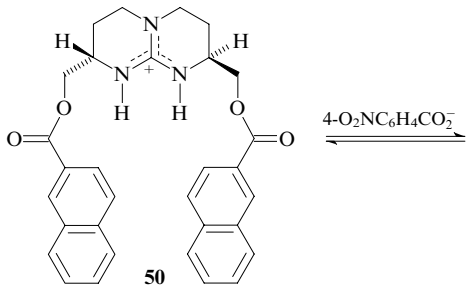


49a,**b**

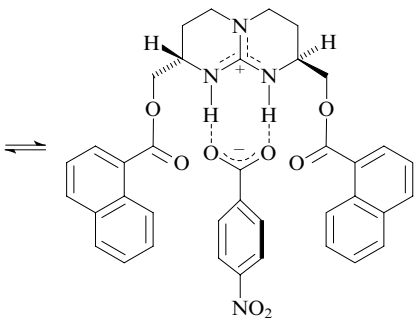
R = Me (**a**), CH_2COEt (**b**).

Compound	R	
	$PhCO_2^-$	AcO^-
49a	5.4×10^2	8.26×10^2
49b	10^3	1.2×10^3

Interesting examples of carboxylate anion binding by ligands containing a guanidinium fragment are also described. For example, upon the interaction of cation **50** with *p*-nitrobenzoate, the chelate structure is formed.[119]

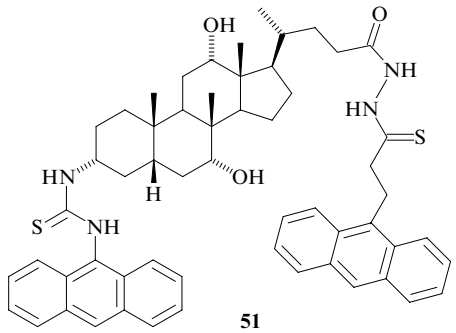


50



Protonated forms of *N*-substituted guanidinocarbonylpyrroles are effective receptors for the carboxylate anions of amino acids ($K > 10^3$).[120]

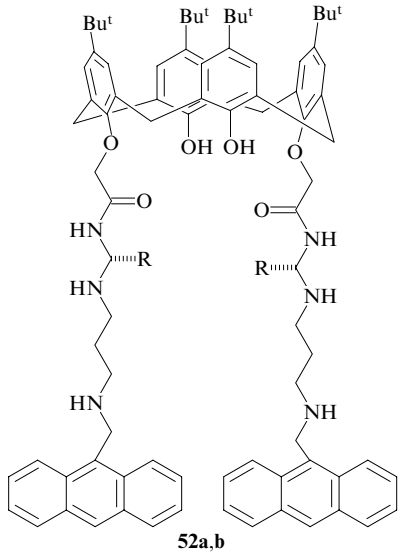
In the recent literature, one can often find examples of receptors for the binding of anions of di- and triatomic carboxylic acid. Thus the high degree of binding with anions of different polyatomic carboxylic acids was found for steroid **51**.[121]



51

Anion	*K*	Anion	*K*
Malonate	9.9×10^4	Isophthalate	2.2×10^4
Succinate	1.7×10^5	Terephthalate	1.3×10^5
Glutarate	2.9×10^5	Citrate	1.5×10^5
Adipate	5.6×10^5	*N*-Acetyl-L-glutamate	1.0×10^6
Suberate	1.9×10^5	L-Glutamate	5.6×10^6
Sebacate	6.5×10^5		

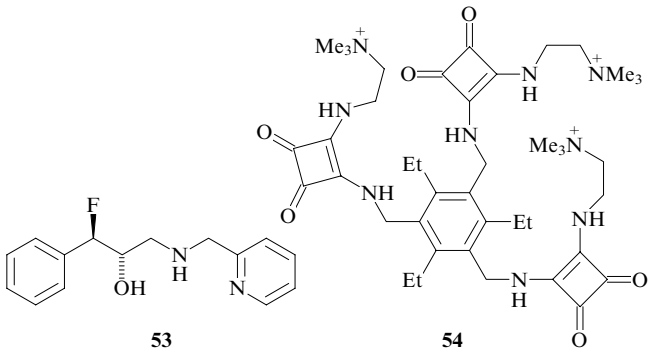
For the recognition of enantiomers of dicarboxylate anions the derivatives of sapphirine can successfully be used.[122] Modification of the lower rim of calixarene by an optically active fragment (compounds **52a**,**b**) leads to the enantioselective recognition of L-malate (dianion of hydroxybutanedioic acid).[123] The ratio of binding constants for D- and L-forms of malate for compound **52a** is equal to 4.34, while for derivative **52b**, 10.41.



52a,**b**

R = Me (**a**), Bn (**b**).

Ligand **53**, despite its relatively simple structure exhibits high receptor ability with respect to enantiomers of mandelic acid (for *S*-enantiomer, $K = 7100$, for *R*-form, 12 700).[124]



53 **54**

It was shown[125] that receptor **54** containing three charged amino groups can be used for the recognition of citrate as a tricarboxylate anion.

In the literature one can find single examples of nitrate binding, *e.g.*, by the ligands based on guanidine[126] or bicyclic cyclophane receptors.[127]

3. Receptors for tetrahedral anions

The present Section contains only recent data, since the majority of earlier papers are summarised in the review published in 2006,[128] which is devoted to the binding of tetrahedral oxyanions.

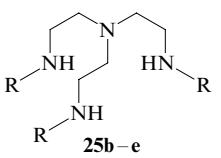
Phosphates and dihydrogenphosphates as well as carboxylates are coordinated by the polyfunctional ligands with molecular cavities of appropriate size containing amide groups or fragments of (thio)urea and others, which can form strong H-bonds.[103] Apart from compounds **13**, **15**, **38**, **41**, considered in the previous Sections, compounds **25b**–**e**, **55**–**60** (Table 4) are used as receptors for binding of dihydrogenphosphate anions.

Table 4. Binding constants of the $H_2PO_4^-$ anion.

Compound	*K*	Ref.
13a	8×10^2	74
13b	5×10^3	74
15a	4×10^3	74
15b	2×10^3	74
25b–**e**	10^3–10^4	129, 130
38	3.4×10^5	103
41	5×10^7	74
55	2×10^3	86
56	–	131
57	1.2×10^4	106
58	2.2×10^5	132
59a	1.5×10^5	133
59b,c	1.9×10^5	134
60	10^4	135

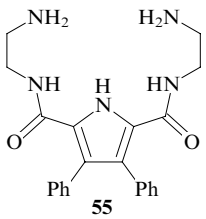
Recognition of $H_2PO_4^-$ ion by the ferrocene-containing receptors is described.[136] Due to the formation of NH···O$^-$ hydrogen bond, free porphyrins bind the dihydrogenphosphate anion (K is in the range of 10^3–10^4).[65,66] According to the data from ^{1}H NMR spectroscopy in acetonitrile and DMF, the unsubstituted calix[4]pyrrole reacts with $H_2PO_4^-$ with the formation of 1 : 1 complexes.[137]

Later, the number of known highly selective receptors for the dihydrogenphosphate anion has increased. For example, sulfamoylcalix[4]arene **61** exhibits 100 times greater binding ability toward the anion $H_2PO_4^-$ compared

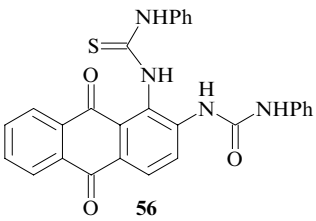


25b–e

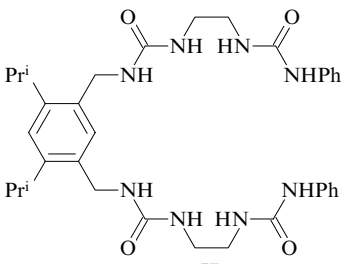
R = $C(O)CH_2Cl$ (**b**), $C(O)C_7H_{15}$-n (**c**), $C(O)C_6H_4NO_2$-3 (**d**), $SO_2C_4F_9$-n (**e**).



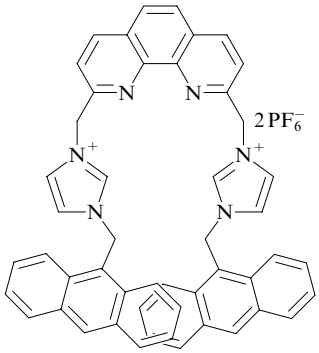
55



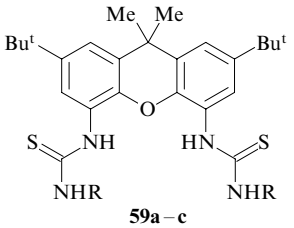
56



57

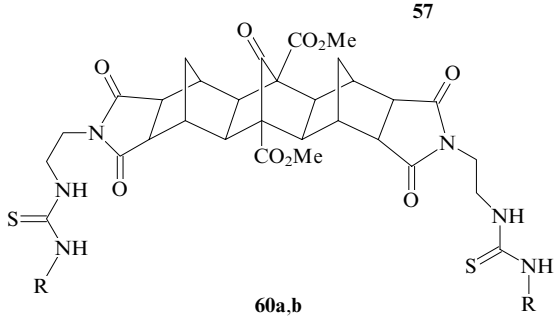


58



59a–c

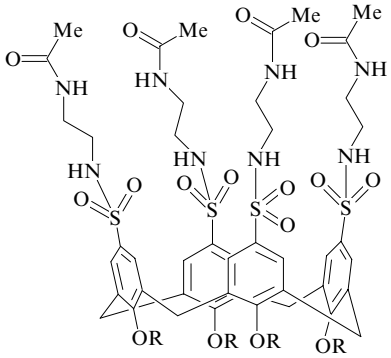
R = Pr^n (**a**), Bu^n (**b**), Ph (**c**).



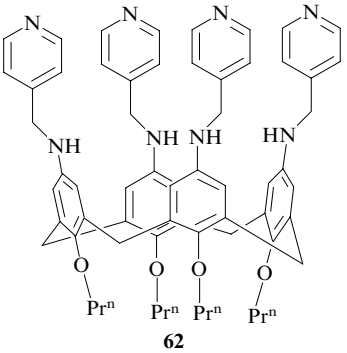
60a,b

R = 4-$F_3CC_6H_4$ (**a**), 4-$O_2NC_6H_4$ (**b**).

to Cl^- and NO_3^- ions.[88] Calixarene **62**, which contains pyridylmethylamino fragments in the upper rim, can also be used to this end. By means of UV spectroscopy it was established[138] that this compound forms stable 1 : 1 complex with the dihydrogenphosphate anion (K = 1770).



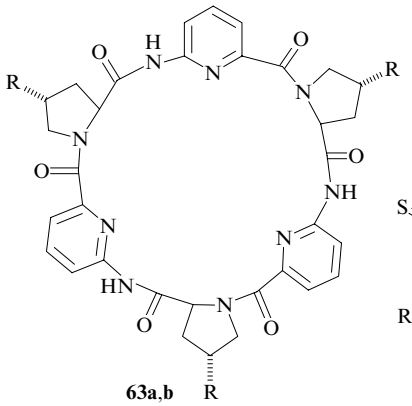
61



62

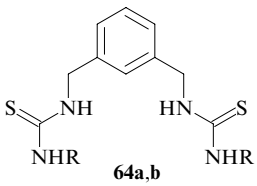
R = $MeOCH_2CH_2$.

The number of examples of binding of the SO_4^{2-} ion is very limited. The most suitable receptors for this anion are cyclopeptides **63a,b** and their dimers which have $K > 10^5$ (Refs 139 and 140). However, compounds with simpler structures modified by thioureido fragments (*e.g.* derivatives **64a,b**) can also be used as effective ligands for binding of the anion SO_4^{2-} ($K = 10^5 - 10^6$).[141]



63a,b

R = H (**a**), OH (**b**).

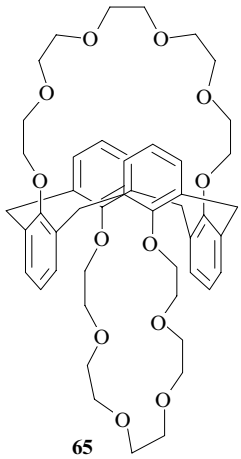


64a,b

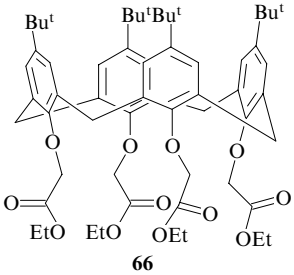
R = Bu^n (**a**), Ph (**b**).

Calixarenes functionalised at the upper rim by amide or amine substituents are suitable substrates for the coordination of the dichromate anion due to the formation of four H-bonds.[142, 143]

In recent years, the number of papers devoted to binding of pertechnetates and perrhenates has greatly increased. This is caused by the urgency of the problem of utilisation of anthropogenic wastewater. For this purpose, calixarenes of various structures can be successfully used. It was shown[144] that calixarene **65** in the *1,3-alternate* conforma-



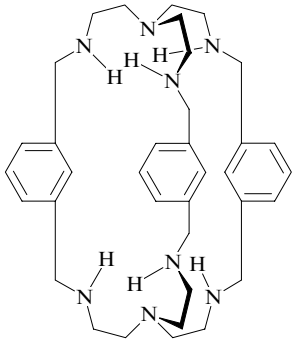
65



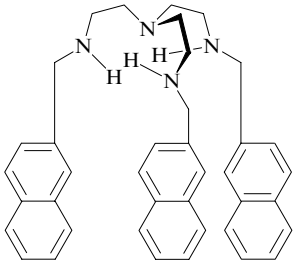
66

tion easily extracts the pertechnetate anions from solutions. And the substituted calixarene **66** which exists in the *cone* conformation and contains ester groups is effective for the selective recognition of ReO_4^- and TcO_4^- in the presence of a number of other anions, Cl^-, Br^-, AcO^-, $H_2PO_4^-$ and NO_3^- (Refs 145 and 146).

Polyamines can also bind the perrhenate and pertechnetate anions. By means of NMR spectroscopy it was shown [29] that the protonated form of polymacrocyclic amine **67** interacts with the perrhenate and pertechnetate anions where $K(ReO_4^-) > K(ClO_4^-)$, and triamine **68** effectively binds TcO_4^- ion.

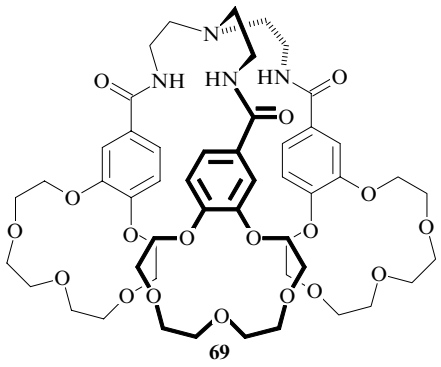


67



68

The tripodal ligand, tris(amidobenzo-15-crown-5) **69**, can be used as a heteroditopic ligand for the recognition of the perrhenate anion together with the sodium cation.[147]



69

* * *

At present, the anion recognition by synthetic receptors is one of the most rapidly developing branches of chemical science. First of all, this is caused by the fundamental role of anions in chemical and biological processes. In the present review it was shown that the binding of a ligand to an anion occurs mainly due to H-bonding, electrostatic interactions, hydrophobic effects and coordination with metal ions. The design of a selective anionic receptor should take into account first of all the geometry of the target anion.

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[b] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*